Thermal Properties and Characterization of Gas Hydrates

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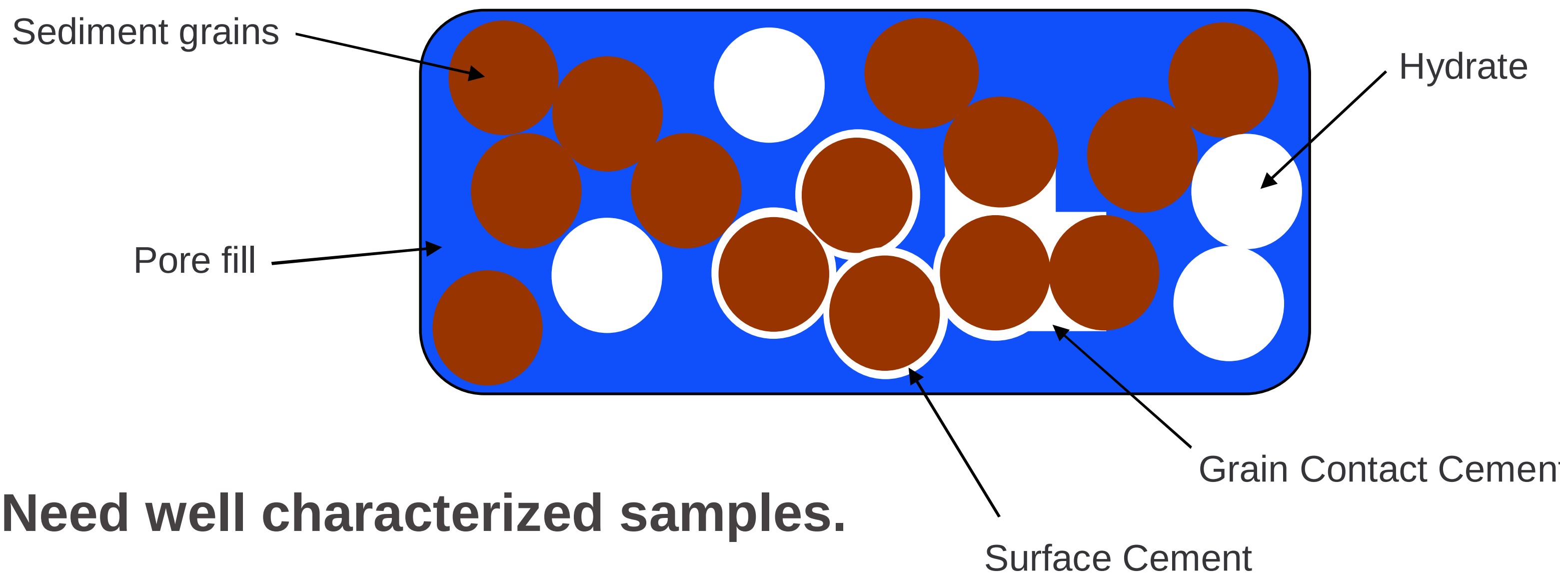
Significance of Present Research

- **Supports the DOE Methane Hydrates Program**
  - Characterization of thermophysical and thermodynamic properties.
- **Thermal properties**
  - Essential to understanding hydrate decomposition and production.
  - Important parameter in…..
    - Predicting resource production.
    - Prevention and removal of hydrates during gas production.
    - Processing and transportation.
    - Climate calculations.

http://en-env.llnl.gov/gas_hydrates/index.html

Measuring Thermal Properties

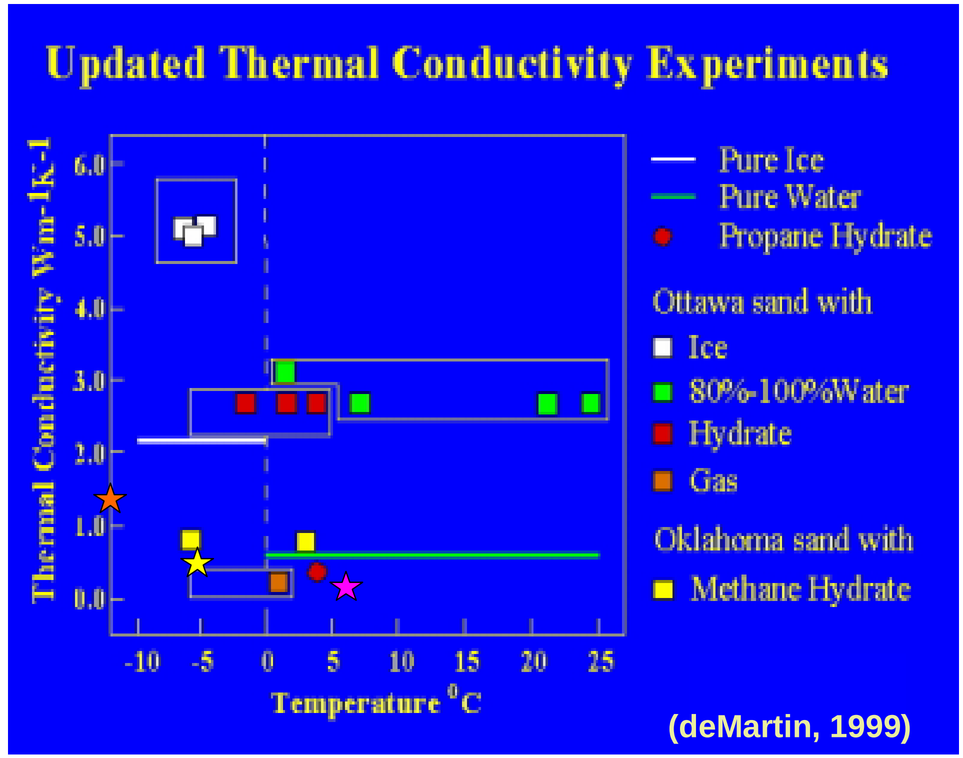
- **The thermal conductivity of an aggregate of sediment, water, and hydrate depends upon:**
  – The conductivity of the individual phases,
  – The concentration and distribution of the phases,
  – The properties of the interfaces between the phases:



- **Need well characterized samples.**

Thermal Conductivity Measurement History

- **Few measurements**
- **Incoherence between investigators**
- **General lack of sample composition information**
  - Need well characterized samples.
- **TC of hydrate is markedly less than that of ice.**
  - Close to that of water.



★ **NETL, 2001, Methane Hydrate**

★ **USGS, 2002, Methane Hydrate**

★ **USGS Woods Hole, 2002, 33% Methane Hydrate/67% Quartz Sand**

NETL Objectives

- **Near Term**
  - Develop experimental equipment and procedures.
  - Obtain physical and thermal property information on gas hydrate samples of known composition.

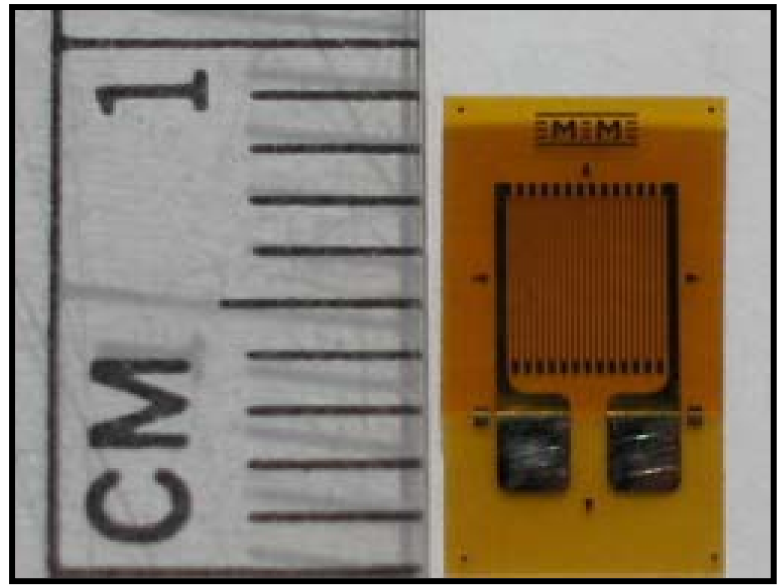
- **Long Term**
  - Provide information useful for developing production strategies for gas hydrates from measurement of important physical, chemical, and thermal properties of carefully prepared and characterized hydrate samples.

Transient Plane Source (TPS) Technique

- Developed and patented by S.E. Gustafsson (1991).
- Used successfully to simultaneously determine thermal diffusivity and thermal conductivity.
- Accurate for a wide range of thermal conductivity values.
- TPS element serves as heat source and temperature sensing element.
- Quick and non-invasive.
- Can be used with small sample sizes.

Experimental System
Transient Plane Source (TPS) Element

- **Commercially available precision strain gauge.**
- **Attached to PVC for support.**
- **Located at sample holder bottom for good contact with the sample.**

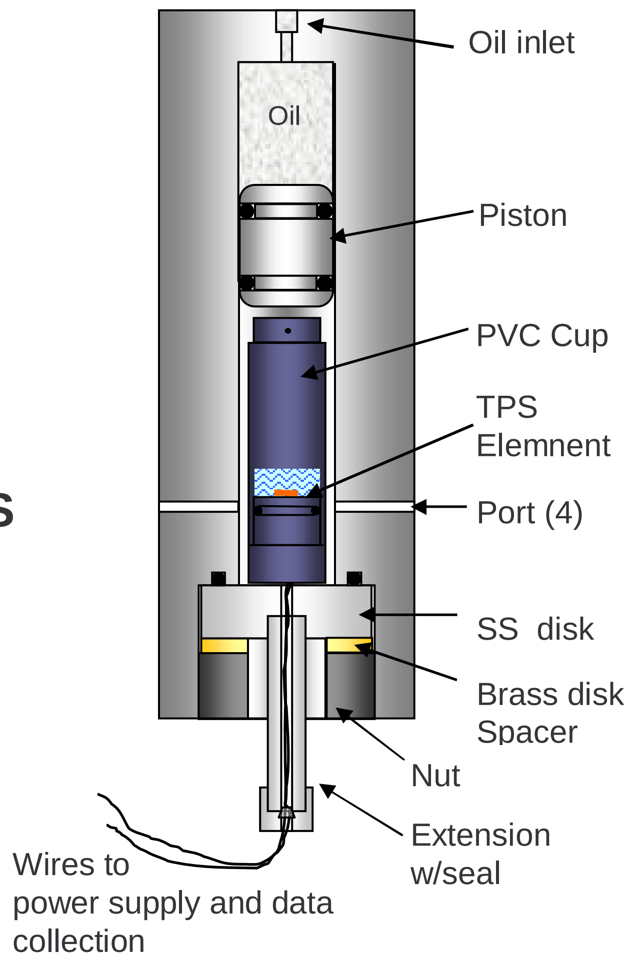


TPS Element

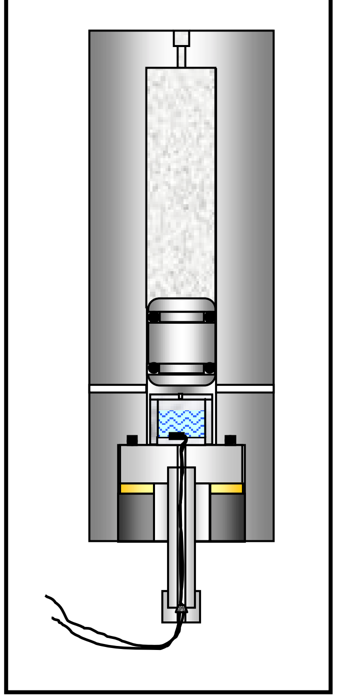
Experimental System
High-Pressure Variable-Volume Viewcell (HVVC)

- **40 ml capacity.**
- **Observations to 6.8 MPa.**
- **Movable piston to change either working pressure or internal volume.**
- **Optional cup with transparent bottom (no TPS element).**
- **Digital Heise pressure gauge and platinum RTD temperature probe.**
- **System was calibrated using glycerol.**

Improved Experimental System



Old System



HVVC with TPS Element

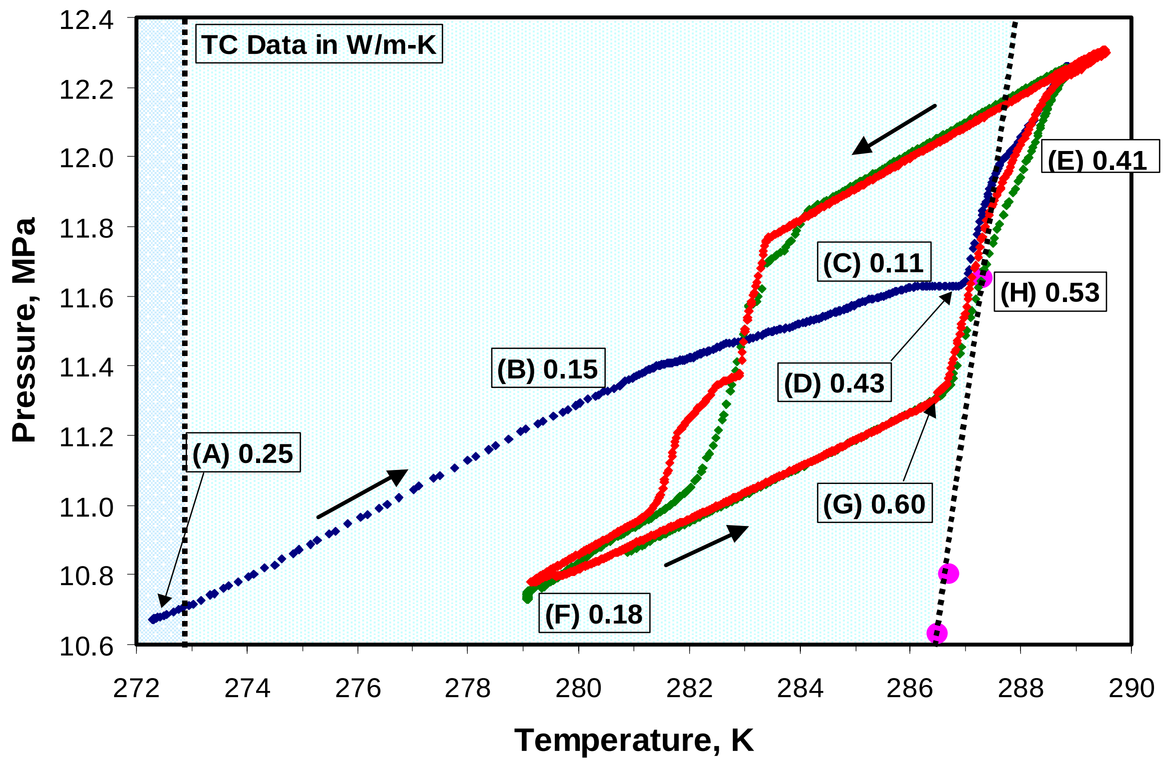
Experimental System
Programmable Environmental Chamber

Environmental chamber and computer system

HVVC mounted inside environmental chamber

Thermal Conductivity Measurements During Hydrate Formation and Dissociation

- **TC data and hydrate observations easily correlated.**
  - Started with ice under helium at 270.8 K; TC=1.60 W/m-K.
  - TC data showed hydrate decomposition before P-T data.
  - TC results low but reproducible for the first three cycles.



- **Obtaining the data was labor intensive.**
  - Recent changes have automated the process.
- **Some water found outside the cup at end of experiment.**
  - New cup holds water and allows for sample recovery.

Data Analysis: Theory

- **Starting with Carslaw and Jaeger's point source solution to the thermal conductivity equation, the temperature rise can be found (for a square conductive pattern of the TPS element):**

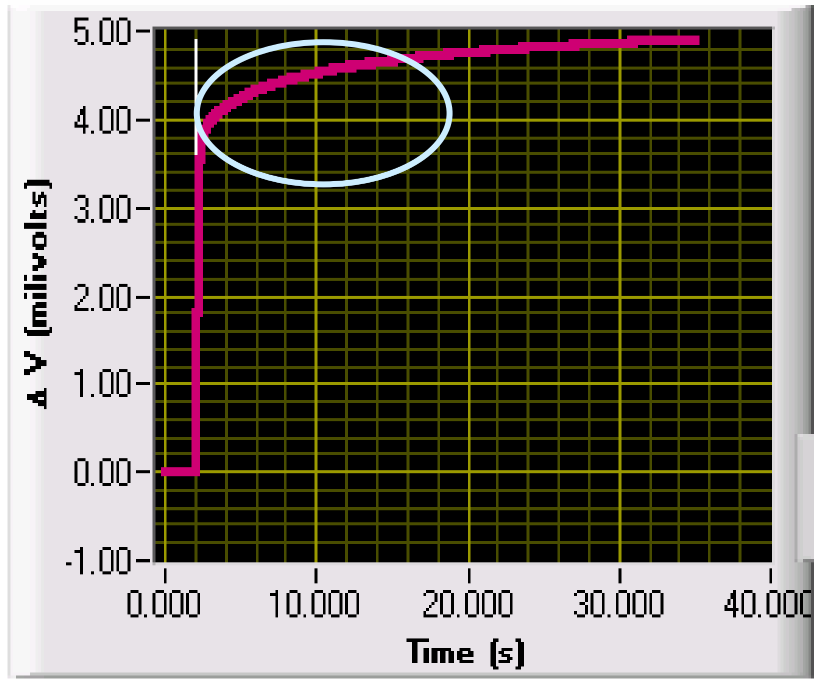
$$\overline{\Delta T(\tau)} = \frac{P_0}{4\pi^{1/2} a k} H(\tau)$$

  - $H(\tau)$ describes the shape of the conducting pattern of the TPS element.
  - k is the thermal conductivity.
  - $2a$ is the sensor width.
  - P_0 is the total power .

- **The temperature rise of the sample is found by recording the voltage difference across a Wheatstone Bridge during a transient heating.**

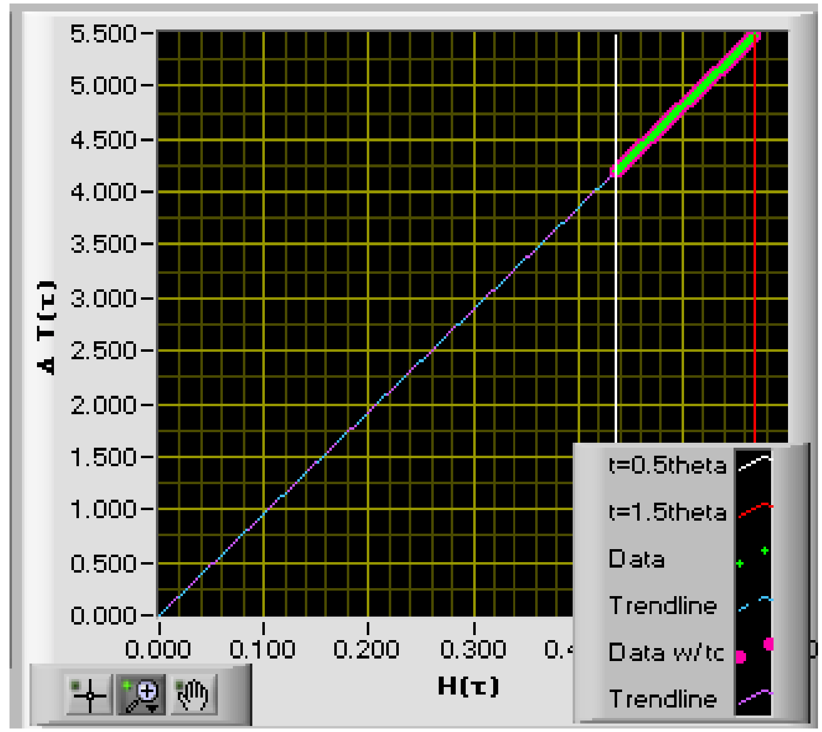
Data Analysis: Raw Data

- **A low voltage is applied to the TPS element.**
  - Heats sample.
  - Temperature sensor.
- **The voltage difference across a Wheatstone bridge is measured with time.**
  - Calculate temperature rise.
- **ΔV versus time data obtained from TPS probe.**
  - Information rich region is used for analysis.
  - The start of the current pulse is influenced by:
    - Non-ideal electrical components
    - Delays in the power release to the sample caused by thermal barriers.
  - A time correction is used to approximate start of current pulse.



Data Analysis: Determining Diffusivity and Calculating Conductivity

- **A numerical method is used to find the diffusivity value that maximizes a linear fit of ΔT versus *H*(τ) through the origin.**
- **The range of data used in the analysis is based on the characteristic time, θ, of the transient measurement.**
- **The slope of this line is used to calculate the thermal conductivity:**



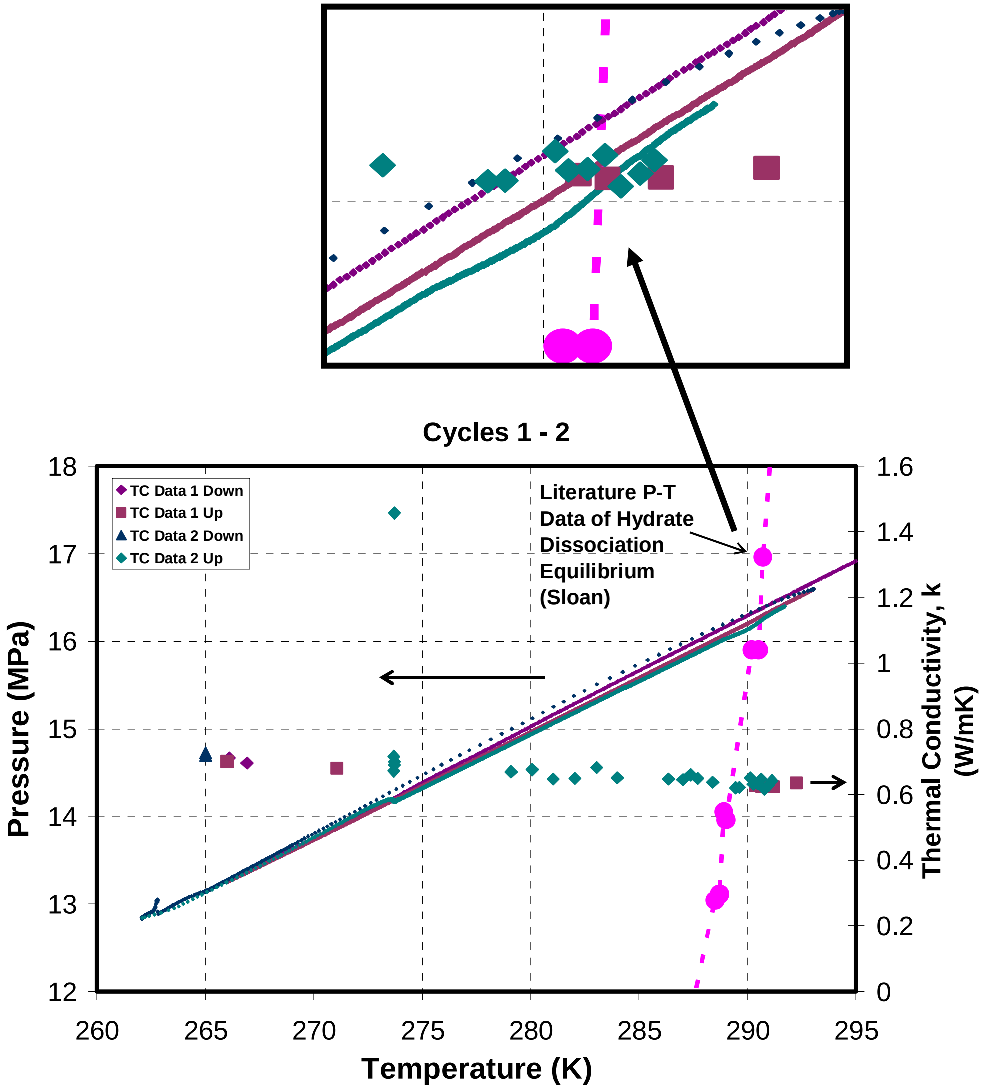
$$k = \frac{P_{avg} s}{4\pi^{1/2} a(slope)}$$

$$\tau = \left[\frac{t}{\theta}\right]^{\frac{1}{2}}$$

$$\theta = \frac{a^2}{\alpha}$$

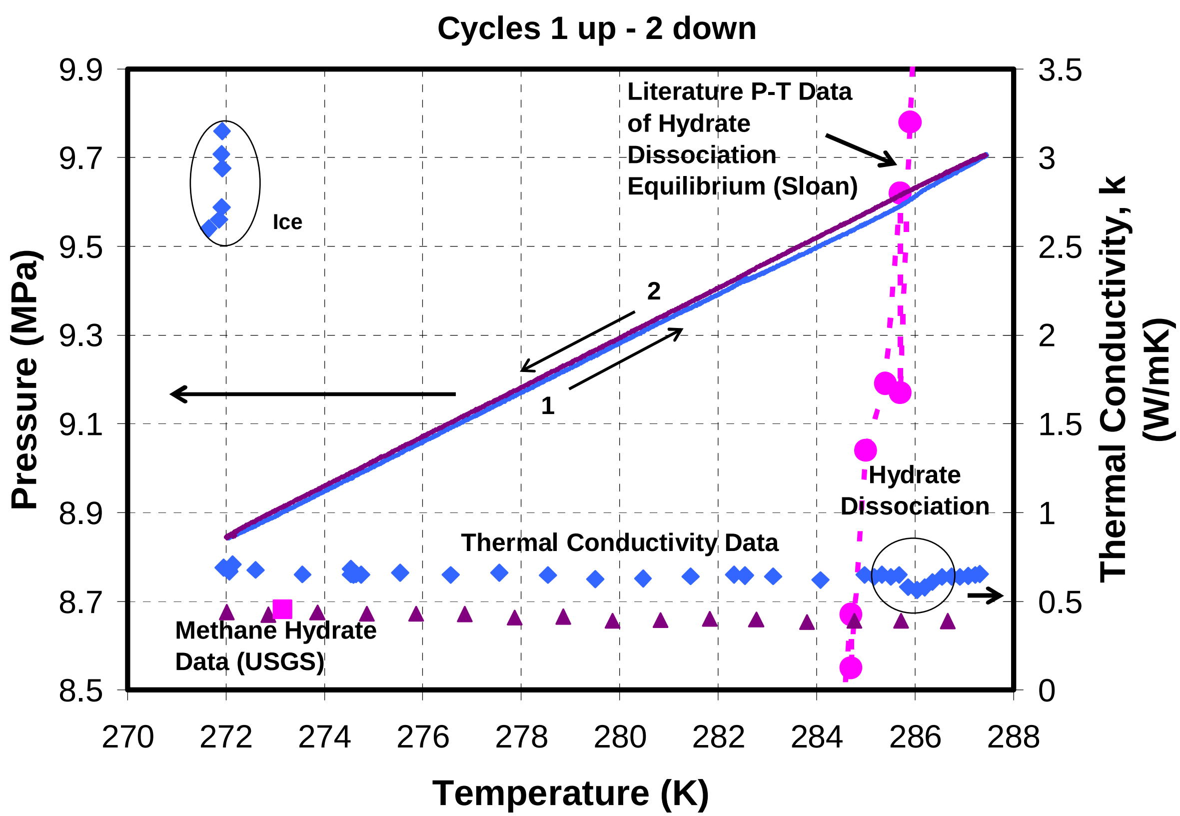
Hydrate Formation from Ice and Methane with TC Measurements

- **Started with 1.41 g of water, k = 0.63 W/mK.**
- **Formed hydrate from ice during cycle 2.**
- **Pressure change due to hydrate formation and dissociation was small.**
- **TC data did not indicate hydrate formation near TPS sensor.**
- **TC measurements drop slightly near hydrate dissociation.**



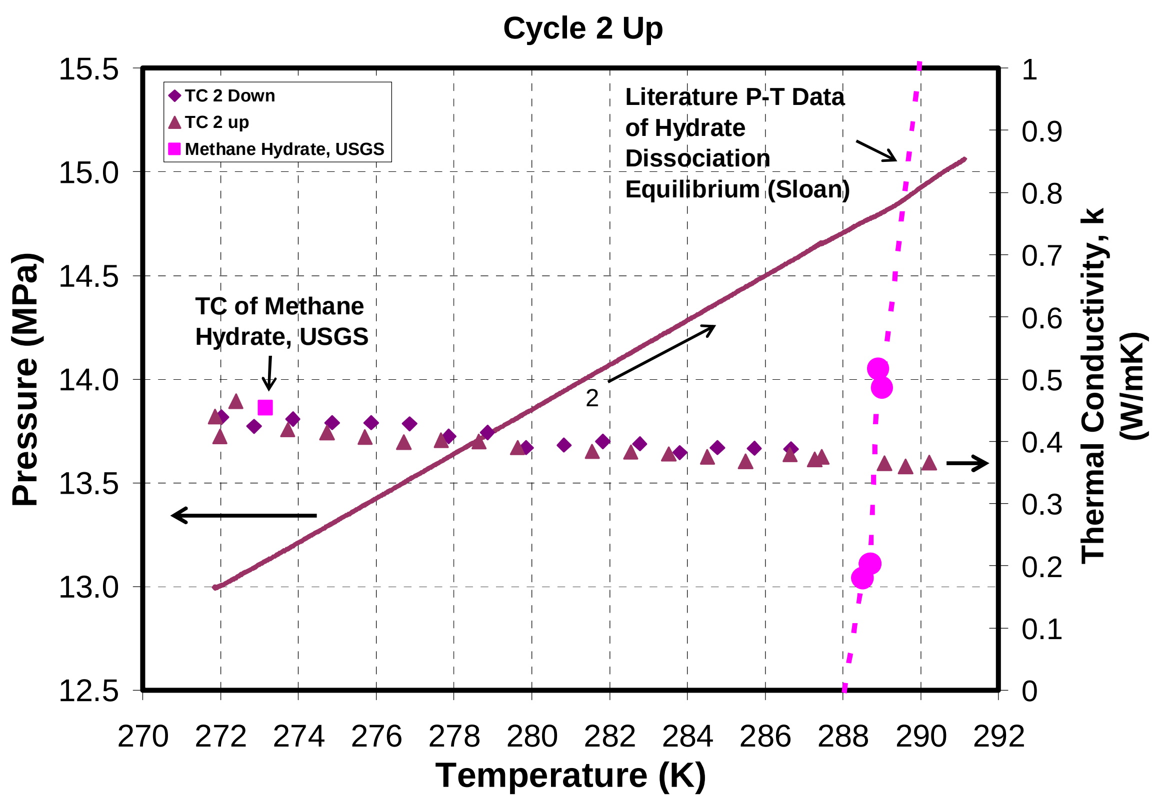
Hydrate Formation from Frost and Methane with TC Measurements

- Started with ~ 1 g of frost from a freezer at ~200 K.
- TC measurements indicate the presence of ice at the start of the experiment.
- The TC values were close to that of water during the first cycle temperature rise.
- Hydrate dissociation was indicated with a decrease in the TC.



Hydrate Formation from Frost and Methane with TC Measurements (cont.)

- The pressure was increased to ~13.1 MPa using the piston.
- TC data indicates hydrate presence.
- Pressure rise due to hydrate dissociation was small.
- TC dropped slightly at hydrate dissociation.



Conclusions

- **The TPS technique has been used to successfully determine thermal diffusivity and thermal conductivity of water, ice and methane hydrate.**
  - Values for water and ice are close to literature values.
  - Thermal conductivity values for methane hydrates are close to those of USGS.
- **Thermal conductivity data give insight into the contents of the cell before P-T data.**
- **Continuing measurements of pure hydrate to further validate new experimental system.**
- **Future experiments will determine thermal properties of hydrate-bearing sediments.**

Acknowledgments

Charles Levander